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IV.

THE QUANTITATIVE DETERMINATION OF ARSENIC, BY THE BERZELIUS-MARSH PROCESS, ESPECIALLY AS APPLIED TO THE ANALYSIS OF WALL PAPERS AND FABRICS.

By Charles R. Sanger.

Presented May 13, 1891.

The original method of Marsh[*] was published in 1836, and in the following year Berzelius[†] proposed the modification which couples his name with that of Marsh. It seems to have escaped notice, at least I can find no mention of the fact, that Berzelius also suggested the quantitative application of the method. He proposed to place some pieces of copper in the reduction tube, and, after weighing tube and copper, to heat and pass the arsenical gas through. The copper would further the reduction of the arseniuretted hydrogen, and thus the arsenic might be collected and weighed. Wöhler,[‡] in 1861, proposes essentially the same method, but heats the tube in two places, at the copper which he uses in the form of a spiral, two inches long, and also just behind the copper, so that whatever gas escapes decomposition by the first heating may be decomposed by the copper. The first practical application of this method seems to have been made by Gautier,[§] in 1876, in the estimation of arsenic contained in tissues. He omits the copper spiral, but heats the reduction tube by a layer of charcoal 20 to 25 cm. in length. To determine the arsenic deposited, he weighs the tube, dissolves out the mirror by nitric acid, and, after drying, weighs again. Crommydis,[‖] a year later, follows Gautier's method in a similar research.

Chittenden and Donaldson,[¶] in 1881, investigated this method with very satisfactory results, and suggested the improvements which

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[*] Edin. Philos. Journ., XXI. 229.

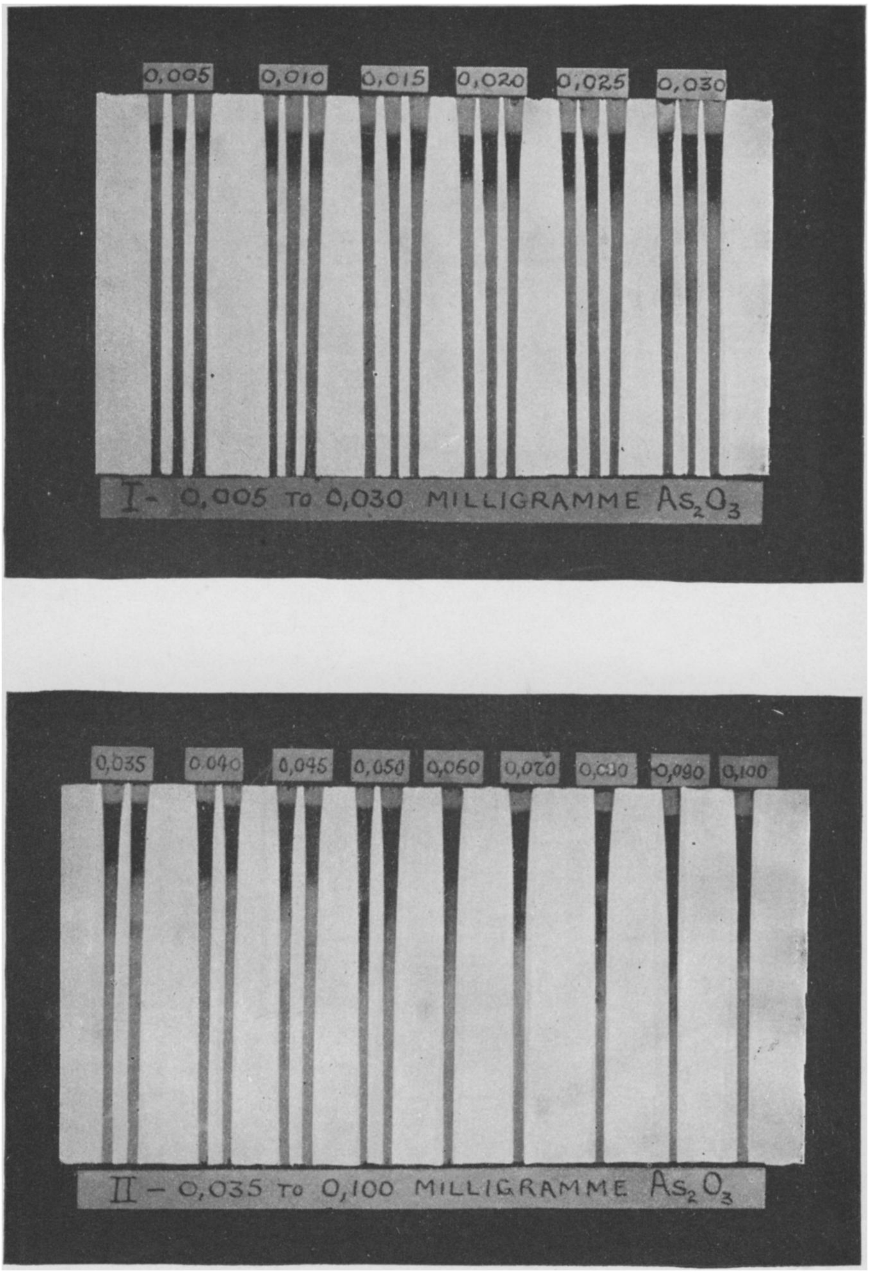
[†] Berzelius, Jahresb., XVII. 191.

[‡] Mineral-analyse, p. 232.

[§] Ann. d'Hygiène publ. et de Méd. légale, 1876, p. 136; also Bull. de la Soc. Chim., [2.] XXIV. 250.

[‖] Bull. de la Soc. Chim., [2.] XXV. 348.

[¶] American Chemical Journal, Vol. II. No. 4; Chem. News, XLIII. 21; Moniteur Scient. de Paris, 1881, p. 227.


0,005
0,010
0,015
0,020
0,025
0,030
I - 0,005 TO 0,030 MILLIGRAMME As_2O_3
0,035
0,040
0,045
0,050
0,060
0,070
0,080
0,090
0,100
II - 0,035 TO 0,100 MILLIGRAMME As_2O_3

QUANTITATIVE DETERMINATION OF ARSENIC BY THE BERZELIUS-MARSH PROCESS
STANDARD MIRRORS.

were necessary for its adoption as a trustworthy analytical method. Their process has found its way into the text-books, and needs no explanation here. I note its use by Hubbard* in 1882, and Prescott† in 1886, and undoubtedly many others have employed it in toxicological work. It seems remarkable, therefore, that the previous application of the process to quantitative work should have escaped the attention of Kühn and Saeger,‡ as well as Polenske,§ to whom they refer as the first to propose the method. Kühn and Saeger's article, published a few months ago, contains nothing new; but as the paper of Polenske is inaccessible to me, I cannot say what modification he may have introduced.

I need not refer here to the numerous quantitative methods which depend on the reduction by nascent hydrogen and absorption of the arseniuretted hydrogen by argentic nitrate, the eventual determination of the arsenic being made from the silver solution in a variety of ways. These methods form a class by themselves, and cannot be included in the Berzelius-Marsh process.

All methods for the estimation of arsenic are open to a common objection; they do not allow the estimation of minimal, or even, with accuracy, of small amounts. It happens so often that a small amount of arsenic must remain unestimated, because unweighable, and only an approximation to the real quantity can be made.

In the qualitative analysis of wall papers and fabrics by the Berzelius-Marsh method, much confusion results from the careless manner of reporting the amount of arsenic which makes its appearance in the reduction tube. The reports, "trace," "small amount," "large amount," are usually made without reference to any standard mirrors, time of heating the reduction tube, or, in many cases, to the amount of substance taken for analysis. On account of the want of a definite quantitative method which could be easily applied to wall papers and fabrics, there have been some propositions for a rough quantitative determination, which should serve as a control as to whether the substance contained more or less than a prescribed amount. The Swedish law || of 1883, for instance, though not using the Berzelius-

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* Physician and Surgeon, Ann Arbor, IV. 348; also, Contributions from the Chem. Lab. Univ. Mich., Vol. I. Part I. p. 12.

† Chem. News, LIII. 79.

‡ Ber. d. deutsch. chem. Gesell., XXIII. 1798.

§ Arb. a. d. kais. Gesundheitsamt, Bd. V. Heft 2 (1889).

|| Correspondence between the English and other Governments respecting the Presence of Arsenic . . . in Wall Papers and Textile Fabrics. Commercial, No. 40 (1883).

Marsh method, prescribes that "440 sq. cm. of the article . . . by reduction with potassic cyanide and sodic carbonate, shall not produce more than a partially opaque mirror in a glass tube of 1.5 to 2 mm. inner diameter." Thoms* in 1883 proposes as a means of control that the results from 100 sq. cm. of paper should be divided into four grades: "strongly arsenical," "arsenical," "traces," and "free." If, when the apparatus has been running ten minutes after the introduction of the solution to be tested, a deposit is obtained no larger than that corresponding to what is produced by 0.1 mgr. of arsenious oxide under similar conditions, the paper may be considered to contain a "trace," and need not be rejected.

A committee of the National Health Association of Great Britain, consisting of Messrs. Bartlett, Heisch, and De Chaumont,† suggested, in 1883, that a paper should be considered non-arsenical if, after being treated by a modification of the Berzelius-Marsh method devised by them, it failed to give a mirror in a tube of one eighth inch internal diameter (about 3.3 mm.) sufficient to cut off at any point a black line of a certain thickness ("thick rule, 8 to pica") on a white ground.

All this is very crude, yet, without a means of easily estimating the amount of arsenic present, it might answer until the exact determination was called for.

The length of time necessary for any of the quantitative methods precludes their use by analysts, especially when, as is generally the case, the quantitative determination is not of especial importance. If we attempt to apply the gravimetric Berzelius-Marsh method to the analysis of wall paper, we are met, not only by the amount of time necessary for the complete deposition of the arsenic mirror, but by the large amount of paper that must be taken, or, if the proportion of arsenic is very small, the unwieldy amount. Added to this is the necessity for a delicate balance, and also the error in weighing small mirrors of arsenic.

A method is therefore desirable which will allow us to estimate minimal amounts of arsenic, and, in such analyses as that of wall paper, will give an approximate idea of the amount present without requiring more time than that needed for the proper conduct of the ordinary Berzelius-Marsh method.

The process which is described in the following pages was suggested by Professor H. B. Hill of Cambridge, about five years ago, and has been in use in that laboratory and others with excellent success. The proof of the availability of the method was undertaken by me, but, owing to numerous interruptions, the completion of the analytical work has been delayed until now.

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* Ref. Fres. Zeitschr., XXII. 474, from Ber. d. landw. chem. Vers. u. Samencontrolstat. zu Riga, 1883.

† Brit. Med. Jour., 1883, p. 1218.

The method consists, briefly, after getting the arsenic from a measured amount of paper or fabric into solution, in the comparison of the mirror obtained from an aliquot part of the solution with a series of standard mirrors obtained from known amounts of arsenious oxide. No method founded on exactly this principle has ever been fully described, though Otto [*] gives cuts of mirrors obtained from known amounts of arsenious oxide, with which some analysts may have compared their mirrors. Selmi,[†] in 1880, states that he is able to approximate to fractions of a milligram by comparing the mirrors with those obtained from the following amounts: one twentieth, one fiftieth, one hundredth, and one two-hundredth part of a milligram. Thoms, as stated above, compares his "traces" with a mirror obtained from one tenth of a milligram, and says that the mirror can be kept any length of time as a comparison standard. Blyth [‡] also suggests a comparison of mirrors.

I give in detail the method as I have used it in the analysis of wall paper, making references to the analytical and experimental work which follows.

The measurement of the paper is governed by (*a*) the quantity of arsenic present, which may sometimes be judged by the color, or by the rough test of the odor from the burning paper, and (*b*) by the character of the paper; i. e. whether a plain color, a small or large figure. I have used 25 sq. cm., 50 sq. cm., and usually 100 sq. cm. As patterns for cutting, thin plates of glass [§] may be used, on which are marked the dimensions. The advantage of the glass is, that the figure of the paper may be seen while the paper is being cut, and also, that, by washing or wiping the glass after each cutting, any danger of contamination by adhering particles from a previous arsenical paper may be avoided. I have used but one plate for 25 sq. cm. (5 × 5); for 50 sq. cm., three (5 × 10, 4 × 12.5, and 2 × 25); and for 100 sq. cm., five (10 × 10, 5 × 20, 4 × 25, 8 × 12.5, and 2 × 50); such a number allowing the variety in cutting that different papers necessitate.

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[*] Graham-Otto-Michaelis, Lehrbuch, II. 2, 520.

[†] Gazz. Chim. Ital., X. 435.

[‡] Poisons, their Effect and Detection, 1884, p. 534.

[§] Dr. Charles Harrington.

The paper, cut into small pieces, is placed in a glazed porcelain dish and moistened with 1 to 5 c. c., according to the amount of paper taken, of strong sulphuric acid (sp. gr. 1.8) to which has been added about one thirtieth of its volume of strong nitric acid (Appendix, 2. *e*). The paper and acid are stirred with a thick glass rod until the paper has absorbed the acid, and the dish is then placed on a ring and heated by a low flame, the mixture being stirred continually, until the paper is thoroughly charred (App., 1). This may be determined by the dry "crumbly" appearance, and by the amount of fuming, it being necessary to heat until the nitric acid is expelled. Usually, the first heating is enough, as, even if a trace of nitric acid is left, it does no harm (App., 2. *f*) ; yet, if one has reason to think that considerable nitric acid is held back, it is best, after cooling, to add a few cubic centimeters of water, and heat again until the fumes of sulphuric acid appear. On cooling, the "char" is moistened with a few drops of water, and then about 5 c. c. of water are added. The mass is triturated with the thick rod until all lumps are thoroughly broken up, heated to boiling to expel sulphur dioxide (App., 5. *d*) and filtered hot (App., 3).

Filtration of the Extract. — In filtering, time is saved and greater accuracy assured by using a filter pump, and for filtration I have found most convenient a sideneck test tube of 25 to 30 c. c. capacity. This is fitted with a rubber cork through which passes a small funnel, the end reaching just below the side tubulus of the test tube. With the tubulus is connected the pump, and in order to prevent accidental contamination of the tubulus, (through which the extract is afterwards poured into the Marsh apparatus,) I use a connecting glass tube, which may be rinsed before and after each filtration. This tube is a small U tube not over 25 cm. in total length, with two bulbs blown in the lower part of the U. The filter paper is of small diameter, not over 8 cm. and the lot should be tested for arsenic previous to cutting the round filters. As a strengthening cone at the apex will be found convenient for this, as well as for other filtrations, a square piece of cheese cloth laid under the paper and folded with it.

After filtering, the char is washed with small quantities of hot water until the filtrate and washings fill the test tube. The extract, after cooling, is ready for weighing or measuring, and introduction into the apparatus.

The Apparatus. — Two points will have been noticed in working with the ordinary form of generating flask: the time required for displacement of the air, and the impossibility of governing the evolution of hydrogen during the analysis. The latter objection is partially remedied by some such contrivance as that of Lehmann* or of Blondlot,† both of whom regulate the current by raising or lowering the zinc by a glass rod working through the cork of the flask. Chittenden and Donaldson ‡ regulate the evolution by the successive use of acids of increasing strength. Both difficulties are, however, obviated by the use of a constant hydrogen generator by which the air of the flask may be swept out and the flow of the hydrogen controlled, thus assuring the uniform rate of deposition of the arsenic, on which the success of the process as a quantitative one largely depends. This idea of a constant generator was apparently first proposed by Verryken,§ and has been used also in 1888 by Wolff ‖ in a modification of Bloxam's electrolytic method.¶ Any form of generator can of course be used. To the delivery tube is attached a distributing tube, which may be two-way or three-way, according to the number of reduction flasks used. For two flasks an ordinary Y tube suffices, each end of the Y being fitted with a thick rubber connecting tube and a screw clamp, so that the supply of hydrogen may be shut off entirely or controlled for each flask. The reduction flask is a wide-mouthed bottle of about 75 c. c. capacity, fitted with a rubber stopper pierced with three holes. Through one hole passes a right-angled tube reaching to the bottom of the flask, the other end being connected with the distribution tube of the generator. Through the second hole passes the right-angled delivery tube, reaching just below the rubber cork. The third hole serves for the introduction of acid and extract. Through it passes to the bottom of the flask a tube with the bore at the lower end somewhat reduced by melting.** In the top of this tube is set a very small funnel.

To the delivery tube of the reduction flask is attached by a rubber stopper a straight bulb drying tube filled with fused calcic chloride (App., 5. *a*), and to the drying tube is connected by a short thick rubber tube the reduction tube, which should be of the hardest and best quality of Bohemian glass (App., 5. *b*), and of as uniform bore as possible, about 7 mm. inside and 8 mm. outside diameter. It should be drawn out before a small blast-lamp flame to as nearly as possible definite bore, which ought to be from 1.5 mm. to 2 mm. at the place of deposition of the arsenic mirror. The finely drawn tube is bent slightly upward, and sealed at the end.

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* Pharm. Zeitschr. f. Russland, 1888, XXVII. 193.

† Mémoires de la Soc. Roy. de Sci., Lett. et Arts de Nancy, 1845.

‡ Loc. cit.

§ Ref. by Dragendorff, Ermittelung von Giften, 1876, pp. 337 and 317, to Jour. de Pharm. d'Anvers, 1872, pp. 193 and 241.

‖ Fresen. Zeitschr., XXVII. 125.

¶ Ibid.; also Blyth, loc. cit., p. 533.

** That the fluid introduced may not carry any air with it into the flask.

The Reagents (App., 4). — The zinc and sulphuric acid used in the apparatus must be *strictly* free from arsenic, and one should not feel satisfied of their purity unless a stream of hydrogen from the generator, led through the heated tube for several hours, fails to give the slightest deposit. The granulated zinc used in the generator is best of comparatively large size, while that used in the reduction flasks should be quite fine-grained. The acid should have a concentration of one part strong acid (1.82 sp. gr.) to eight parts of water, though a more dilute acid can often be used.

The Course of Analysis. — In the reduction flask is placed a small quantity, not over three grams, of zinc, and the apparatus is connected together. Tightness must be assured, and can be tested for, if the tip of the reduction tube is sealed, by adding through the small funnel a few drops of acid. If these do not fall, the tip of the tube is broken off, leaving an opening of not more than 1 mm. diameter, and then about 20 c. c. of acid are added. The hydrogen is now turned on from the generator, and, after expulsion of the air, lighted, and the flame turned down to a height of 1 to 2 mm. The evolution of hydrogen should be kept at this rate during the reduction of the arsenical solution. Often it is not necessary to use the generator during the reduction, as the evolution from the reduction flask is sufficiently rapid. If it slackens, the generator may be used again, and indeed it is generally necessary to use it toward the close of the reduction. It may happen, on account of too strong acid or increased action after introduction of the extract, that the evolution is too rapid, and the flask becomes heated (App., 5. *c*). To obviate this, the flask may be set in a vessel fitted with an exit tubulus, and filled with cold water, which can be drawn off and replaced when necessary without disturbing the apparatus. An ordinary crystallizing dish with a siphon would answer the purpose.

Shortly after (App., 5. *e*) lighting the hydrogen, the lamp is placed under the heating place and the apparatus tested for absence of arsenic for such length of time as the circumstances direct. In ordinary analyses of wall paper, I allow 15 to 20 minutes' free run before adding the extract.

The lamp should give a large clearly defined flame (App., 5. *f*), and should heat the tube with its oxidizing flame only. An iron cone may be used for increased draught, but not an iron or glass cylinder, for the greater radius of heat given by the latter tends to throw the mirror farther along the tube, and to deposit it irregularly. A convenient rest for the reduction tube is made by soldering three stout copper wires to an old binding screw or post, curving the ends to fit the tube and branching them out, so that the tube lies flat in the curved ends. The binding screw travels vertically on a brass rod melted into a flat, heavy piece of lead, or screwed into the base of an old Bunsen burner.

When the apparatus is found free from arsenic, the extract is added. Previous to this it has been measured or weighed, preferably the latter. The test tube having its weight marked on it, the weight of the extract is quickly determined. Weighings can be made on a balance sensitive to fifty milligrams, which is enough for all practical purposes.

A few drops of the extract are at first added. If no mirror appears in three or four minutes, one eighth to one quarter of the rest may be added, and if in five minutes more there is no mirror, the whole of the extract may be introduced. This cautious addition is necessary in order not to obtain too large a mirror, else a difficulty in estimation might arise, or a new determination might have to be made. A twenty-five minute run is sufficient for the deposition of all the arsenic when the size of the mirror formed in the first fifteen minutes is not larger than that corresponding to 0.05 mgr. of arsenious oxide. If the mirror forming is likely to be larger than this, it is better, after weighing, to start another mirror with another portion of the extract, than to wait for the complete deposition of a mirror which may be too large for comparison with the standards.

The set of standard mirrors is made as follows. One gram of arsenious oxide, purified by repeated sublimation, is dissolved with the aid of a little sodic bicarbonate (free from arsenic), and, after acidification with dilute sulphuric acid, is made up to a litre. Of this standard solution (I.), containing 1 mgr. As_2O_3 to 1 c. c., ten c. c. are taken and made up to a litre, giving the standard solution (II.) containing 0.01 mgr. to 1 c. c. Of this solution, 1 c. c., 2 c. c., 3 c. c., etc., are carefully measured from a burette and introduced into the reduction flask of the apparatus, giving the mirrors corresponding to the same number of hundredth-milligrams. It is necessary to make two or more mirrors of the lower amounts, as, even with careful drawing, the cross sections of the deposition tubes differ, so that the appearance of the mirror from the same amount of arsenic varies, and the variation is more marked as the mirrors decrease in size. Then, for greater convenience in interpolation, mirrors corresponding to the half-hundredths may be made, so that the set which I use contains the following amounts: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, and 0.06. Above 0.06 the difference between the mirrors is so hard to estimate with accuracy, that it is of no advantage to make any above 0.06. Yet in the set which I have photographed, and which is shown in the plate, the following are added for comparison: 0.07, 0.08, 0.09, 0.10.

When the set is not in use, it should be kept in the dark, and at *no* time be exposed to direct sunlight. Although the tubes be sealed, yet there is sufficient air inside to cause a rapid oxidation in direct sunlight, especially with the lower amounts, and a film of arsenious oxide results. By observing this precaution, the set can be kept a long time without alteration.

The readings of the mirrors are far sharper by transmitted than by reflected light, and comparison should always be made by the former. For this purpose I use, at the suggestion of Professor Hill, a small tin box painted black on the inside and outside, and similar in shape and construction to the old-fashioned stereoscopic camera. The height of the box is 20 cm.; width, 7.5 cm.; length at top, 10 cm.; length at bottom, 15 cm. The bottom is open, while the top is covered, and fitted with two eyeholes, 2 cm. in diameter and 4 cm. apart. The set of standard mirrors, as shown in the plate, is mounted, by means of sealing wax, in blackened wooden frames, 18 cm. long by about 7 cm. wide, and 4 to 5 mm. thick. The inner dimensions of the frames are 12 cm. by 4.5 cm. The bottom of the box carries a rabbet of tin, on which the frames may be slid, thus bringing the mirrors under the eyeholes. A second rabbet above the first allows the introduction of a frame carrying the mirror to be compared, which may thus be brought between any two of the standards and compared just as in nesslerization. The box is mounted over a white paper or plate, in front of a good light. The calculation of the amount of arsenic in the area of paper taken follows from the determination of the amount in the aliquot part of the solution. From this can be found the number of milligrams per square meter, which, when multiplied by the factor, 0.0128, gives the number of grains per square yard.

APPENDIX. — ANALYTICAL AND EXPERIMENTAL WORK.

The experimental work in the investigation of the availability of the method is given in detail in the following pages.

1. *Necessity of Charring.* — Considerable difference of opinion exists as to the necessity for insuring the absence of organic matter in the extract to be tested. Odling,[*] in 1859, in testing for arsenic in tissues, found that he could obtain arsenic by Reinsch's test in the presence of organic matter, but not by Marsh's. After getting rid of the organic matter by distillation with hydrochloric acid, he had no difficulty with the Marsh test. Blondlot[†] calls attention to the necessity of completely destroying the organic matter. Chittenden and Donaldson,[‡] on the other hand, were able, in the presence of organic matter, to detect very small amounts of arsenic, and consider it of no hindrance. My experience has been, that, while the organic matter may not completely prevent the deposition of small amounts, and is no hindrance in the detection of large amounts, yet the character of the mirror is so altered that comparison with the standards is impossible. Besides, the organic matter causes an increased and irregular flow of gas which tends (App., 5. *f*) to carry undecomposed arseniuretted hydrogen out of the tube. I therefore take the precaution, by thoroughly charring, to insure the absence of organic matter in the extract.

Thoms[§] digests 100 sq. cm. of the paper on the water bath with (1–7) sulphuric acid, and adds the filtrate directly to the reduction flask. Fleck[||] considers that digestion with a 25 per cent sulphuric acid is sufficient to extract the arsenic completely, and Reichardt[¶] concurs in this opinion. I cannot agree with this, and consider that the chance of the arsenic being held as arsenious sulphide is alone enough to condemn the method (App., 2. *c*), not to speak of the organic matter extracted.

2. *Use of an Oxidizing Agent in Charring.* — In case the paper contains chlorides, it seemed likely that a portion of the arsenic would be volatilized during the treatment with sulphuric acid. This was

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[*] Guy's Hospital Reports, V. 367–374.

[†] Loc. cit.

[‡] Loc. cit.

[§] Loc. cit.

[||] Rep. analyt. Chem., 1883, Heft 2.

[¶] Archiv d. Pharm., CCXXI. 271.

found to be true to an extent sufficient to warrant the precaution of adding a small quantity of nitric acid to the sulphuric acid, in order to prevent the formation of arsenious chloride.

a. The Presence of Chlorides in Wall Papers. — In order to determine to what extent chlorides exist in wall papers, several analyses were made of papers taken at random. The method was as follows. A measured amount of paper (400 sq. cm.) was thoroughly moistened with a strong solution of potassic nitrate (free from chlorine) on a broad porcelain plate, dried on the plate, and ignited over the plate. The organic matter was practically destroyed. The residue was transferred from the plate to a chlorine free filter, and washed thoroughly with hot water. The filtrate, after acidification with dilute sulphuric acid, was boiled to expel nitrous acid, and, after cooling, titrated according to Volhard with approximately hundredth-normal solutions. There is no danger of volatization of hydrochloric acid even on prolonged boiling, as Gooch and Mar* have shown that a solution containing 0.12 per cent of hydrochloric acid can be boiled down one half without appreciable loss. In titrating, as well as in determining the strength of the standard solutions, it was found that the dilution of the solution affected the end reaction in that the color of the ferric sulpho-cyanate was obscured by that of the argentic chloride, even if the latter were made to "clump together." This difficulty was easily obviated by heating to boiling after adding excess of argentic nitrate, filtering off the chloride, and titrating back in the cooled filtrate. The end reaction was then as sharp as possible.

Analysis of thirteen papers gave an average of 138 milligrams of chlorine per square meter, or 1.38 mgr. in the usual amount (100 sq. cm.) taken for the determination of arsenic. The highest amount was 238 mgr., the lowest 56 mgr. In no case was a paper found free from chlorides.

b. Effect of Chlorides. — A solution of sodic chloride free from arsenic was made up of such strength that 1 c. c. contained 1 mgr. chlorine. Several trials were made of the effect of a known amount of chloride on small amounts of arsenic. 100 sq. cm. S. and S. filter paper (589) were used in each case. After addition of the arsenic and sodic chloride solutions, the paper was dried in the evaporating dish, and the arsenic determined exactly as described, but without using nitric acid. The following table shows the results obtained.

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* Amer. Jour. Science, [3] XXXIX. 293.

Analyses 1–6 were made with duplicate readings which agreed closely.

	Mgr. As_2O_3 taken.	C.c. NaCl, mgr. Cl, taken.	Mgr. As_2O_3 recovered.	Per Cent As_2O_3 recovered.
1	10.0	20.0	5.22	52.2
2	10.0	20.0	4.96	49.6
3	5.0	4.4	3.61	72.2
4	0.5	2.0	0.44	88.0
5	0.1	2.0	0.87	87.0
6	0.05	2.0	0.02	40.0
7	0.01	2.0	0.005	50.0

Analyses 1 and 2 show that the presence of twice the theory of chlorine causes a large loss, with an amount of arsenic comparatively large. Analysis 3 shows a marked loss with less than the theory. Analyses 4 to 7 were made with more chlorine than the average found (1.38 mgr.), but less than the greatest amount (2 38 mgr.); the amounts are respectively 4, 20, 40, and 200 times the theory, and the conditions are more nearly those met with in practice than in analyses 1 to 3. It will readily be seen that the loss is sufficient to warrant the precaution of using an oxidizing agent.

c. Loss by Retention of Arsenic in the Char as Arsenious Sulphide. — The presence of the sulphide in papers is not very common. Yet papers colored with ultramarine occur frequently, and the sulphuretted hydrogen set free from this by the sulphuric acid acts on the arsenic compound, and thus a large part of the arsenic remains in the char as the sulphide, insoluble in dilute sulphuric acid. The following analyses of a paper are sufficient to show the danger of loss from this source. The paper had a light blue ground, and the odor of sulphuretted hydrogen was apparent on addition of sulphuric acid. 100 sq. cm. charred with sulphuric acid and a few drops of nitric acid gave an amount of arsenic corresponding to 5.9 mgr. per square meter. 100 sq. cm. charred with sulphuric acid alone gave 4.5 mgr. per square meter. The char was then extracted with ammonia, and the extract evaporated with sulphuric acid and a drop of nitric acid. This yielded 0.01 mgr., corresponding to 1 mgr. per square meter and bringing the total amount up to 5.5 mgr., which agrees with the first analysis.

d. The Deposition of Arsenic from a Solution of Arsenic Acid. — The question arises whether the conversion of the arsenious to arsenic acid by use of an oxidizing agent would cause the arsenic to be held back. This was quickly determined by comparison of the standard mirrors with a set prepared from a solution of arsenic acid, of which

1 c. c. contained 0.01 mgr. As_2O_3, as As_2O_5. The mirrors agreed sharply. This is at variance with the results of Headden and Sadler,[*] who found, in using the method of Chittenden and Donaldson, that it was necessary to subject the arsenic acid to preliminary reduction in order to obtain all the arsenic present. The reason for this is, probably, that a very small quantity of arsenic acid, such as would occur under the conditions of this method, is more quickly reduced by nascent hydrogen, while the comparatively large quantity used by Headden and Sadler would take more time. They do not show that prolonged treatment in the Marsh reduction flask would not have eliminated this error.

e. The Use of Nitric Acid as an Oxidizer. — Nitric acid suggests itself at once as the most convenient oxidizing agent. In this connection may be mentioned the method proposed by Blyth,[†] which consists in soaking the paper in potassic chlorate, drying, burning, and extracting with water. Hager [‡] substitutes sodic nitrate for the potassic chlorate. Many destroy the organic matter by hydrochloric acid and potassic chlorate, as in the case of tissues. Lyttkens [§] uses sulphuric acid and potassic chlorate, and Lenz,[‖] commenting on this, considers it the best means of treatment of the paper. The German law [¶] of 1888 prescribes the treatment of fabrics with strong hydrochloric acid and distillation with ferrous chloride. None of these methods in the analysis of wall papers and fabrics have any advantage over charring with the simple addition of nitric acid, and all require more time.

That all the arsenic may be recovered when nitric acid is used is shown by the following: 0.01 mgr. arsenious oxide was added to 100 sq. cm. of filter paper and a drop of strong nitric acid added before charring. The mirror obtained corresponded to 0.01 mgr.

1 mgr. As_2O_3 and 5 cc. sodic chloride solution (5 mgr. chlorine) were added to 100 sq. cm. filter paper and treated with a mixture of one part nitric to six parts sulphuric acid. Duplicate readings gave 1.095 mgr. recovered, an error no greater than that which might occur from the method.

10 mgr. As_2O_3, as As_2O_5, were added to 100 sq. cm. filter paper, and

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[*] Amer. Chem. Journal, VII. 338; Ber. d. deutsch. Chem. Gesell., XIX. 116.

[†] Loc. cit., p. 532.

[‡] Pharm. Centralhalle, XIII. 145.

[§] Ref. Fres. Zeitschr., XXII. 147, from Landw. Versuchsstat., XXVI. 305.

[‖] Fres. Zeitschr., XXII. 147.

[¶] Ibid., XXVII. 471.

treated with sulphuric acid alone. Duplicate readings gave 9.94 mgr. recovered.

Finally, 100 sq. cm. of a wall paper containing no arsenic was, after addition of varying amounts of As_2O_3, charred with a nitrosulphuric acid containing one part nitric to thirty of sulphuric acid. The following table shows the results of four analyses. The readings on 2, 3, and 4 were in duplicate.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 found.	Mgr. per Sq. Meter taken.	Mgr. per Sq. Meter found.
1 . . .	0.01	0.009	1.0	0.90
2 . . .	0.10	0.0995	10.0	9.95
3 . . .	1.00	0 977	100.0	97.70
4 . . .	10.00	10.30	1000.0	1030.00

f. Effect of Free Nitric Acid in the Reduction Flask. — Rieckher* does not consider the presence of free nitric acid to be detrimental, while Fresenius † takes the opposite ground. Blondlot ‡ thinks that free nitric acid gives rise to the formation of a solid hydride of arsenic on the zinc, thus causing the retention of part of the arsenic. Without discussing the correctness of this statement, which seems to have been quite universally accepted, we have only to consider the effect of a trace of the acid on the deposition of the mirror, as the method of charring would leave, at most, but a very small amount of free nitric acid in the extract. 0.02 mgr. and 0.05 mgr. As_2O_3 were added to the reduction flasks in which were about 20 c. c. dilute sulphuric acid, and immediately afterward a drop of strong nitric acid was added to each. The dilution was considerable, but not so great as might occur in practice. The mirrors were clearly defined, and corresponded sharply to 0.02 mgr. and 0.05 mgr. respectively.

3. *Extraction of the "Char."* — It is necessary that the char should be thoroughly pulverized and extracted with *hot* water. Considerable loss is likely to occur if these precautions are disregarded, as the following results show: —

To 100 sq. cm. of a wall paper free from arsenic, 1 mgr. As_2O_3 was added, and the char was extracted with 30 c. c. cold water. 0.77 mgr. were recovered, = 77 per cent.

To the same amount of paper 5 mgr. were added, and the char extracted with 30 c. c. cold water. 3.82 mgr. were recovered, = 76.4 per cent.

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* Neues Jahrb. f. Pharm., XX. 3.

† Fres. Zeitschr., II. 389.

‡ Comptes Rendus, LVII. 596.

To the same amount of paper 10 mgr. were added, and the char extracted as before, but, in addition, the particles were well triturated. 9.19 mgr. were recovered, = 91.9 per cent.

That this loss was not due to error in estimation of the mirrors was shown by repetition of the first two trials, mirrors being obtained from separate portions of the same extract. The char was triturated in each case: —

1 mgr. As_2O_3 gave 0.9 mgr. and 0.9 mgr. Average, 90%.
5 " " " 2.92 " " 2.95 " " 58.60%.

That arsenic would be left in the char was shown as follows: 100 sq. cm. of paper as above, after addition of 5 mgr. As_2O_3, were charred, and the finely ground mass extracted first with cold water. 3.11 mgr. were recovered, = 62.2%. The residue was then extracted with 30 c. c. hot water. 1.63 mgr. were recovered, = 32.6%. A third extraction with hot water gave a solution free from arsenic. Total amount recovered, = 4.74 mgr. = 94.8%.

The quality of the paper has no effect on the loss: 5 mgr. As_2O_3 were added to 100 sq. cm. filter paper and treated as before. Two readings from the same cold extract gave 3.51 and 3.46 mgr. respectively. Average, 69.9%. Finally, to show the practical completeness of extraction with only 25 to 30 c. c. hot water, 100 sq. cm. of filter paper were charred with different amounts of arsenious oxide.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 recovered.				Per Cent As_2O_3 recovered.
		Extract 1st.	2d.	3d.	Total.	
1 . . .	5.0	4.99	0.08	0.0	5.07	101.4
2 . . .	5.0	4.98	0.07	0.0	5.05	101.0
3 . . .	10.1	10.65	0.06	0.0	10.71	106.7
4 . . .	10.0	10.37	0.0	—	10.37	103.7

10 mgr. of arsenious oxide per 100 sq. cm. of paper would correspond to 1,000 mgr. per sq. meter, which is an unusual amount. Hence any smaller amounts would be easily extracted. It should be borne in mind that the error is necessarily great in such large amounts, for the deposit which is compared with the standards is so small a proportion of the total amount that a slight difference in reading is proportionally increased.

4. *Reagents.* — Many chemists prefer to use hydrochloric acid instead of sulphuric acid, on account of the quicker action of the former on the zinc. Opinions vary considerably as to the error arising from volatization of zincic chloride, and consequent deposition at the heating

place, when hydrochloric acid is used. Liebig,[*] very soon after the publication of Marsh's method, called attention to possible error from this source, and several years later Wackenroder[†] confirmed Liebig's opinion. Beckurts [‡] claims that there is no danger to be feared, but does not show conclusively that this is the case. Brescius [§] recognizes the chance of error, and recommends passing the gas through sulphuric acid, if hydrochloric acid is used for generation. The committee of the British Health Association, above referred to, recommends the use of hydrochloric acid, without comment on its possible disadvantage.

While the volatilization of zincic chloride might not interfere with the detection of arsenic in considerable quantity, yet it is of primary importance in this method for the mirror to be of arsenic alone, and hence capable of comparison with standards. We cannot, therefore, run the risk of the small mirror being contaminated by any impurity whatever. For this reason, if for no other, the use of hydrochloric acid is wholly unadvisable. Then the time gained in using hydrochloric acid is not to be considered in this method, as the use of a constant generator reduces the time of analysis so decidedly.

The same desire to hasten the evolution of hydrogen in the ordinary Marsh process has led to the addition of stimulants to the action in the shape of platinic chloride or cupric sulphate. Bernstein [||] has shown that the use of platinic chloride is inadmissible, because arsenic is thereby held back. At the same time, however, he finds no loss when the zinc is platinized or silvered before being used. Headden and Sadler [¶] agree with Bernstein in the case of platinic chloride, and find that cupric sulphate also causes a loss. They also get low results by using a spiral of platinum wire in contact with the zinc. Here, again, the use of the constant generator precludes the necessity for increasing the sensitiveness of the zinc.

Mohr,[**] in 1837, called attention to the fact that the residual zinc even after careful washing contained arsenic. This would seem to substantiate the statement of Blondlot, quoted above, concerning the solid hydride of arsenic. Fresenius [††] also considers that the effect of nitric acid is due to the formation of a hydride. When we consider the case of the mere detection of arsenic by the Marsh process, where all the arsenic is not necessarily reduced to arseniuretted hydrogen, it is quite possible that part is left in the zinc, especially if the extract be not free from nitric acid. But in this method, where all of a very small amount of arsenic is to be reduced, and the action is pushed as far as possible, the probability is that no arsenic is left in the zinc. I have often, after deposition of the mirror, pushed the action as far as the complete solution of the zinc, and have never observed any increase of the mirror at the close. It would seem hardly possible for the solid hydride to remain in that state in a reducing medium for such a length of time (compare also 2. *f*). A large amount of carbon in the zinc is apt to cause too rapid evolution, but I cannot confirm the statement of Headden and Sadler [*] that zinc containing carbon causes a loss of arsenic, and that the zinc must in consequence be free from carbon.

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[*] Ann. d. Chem. u. Pharm., XXIII. 217.

[†] Archiv f. Pharm., LXX. 14.

[‡] Ibid., CCXXII. 653.

[§] Dingl. Polyt. Jour., CLXXXVI. 226.

[||] Inaug. Dissertation, Rostock, 1870.

[¶] Loc. cit.

[**] Ann. d. Pharm., XXIII. 217.

[††] Loc. cit.

5. *General Precautions.* — *a. Means of drying the Hydrogen.* — The use of sulphuric acid is not allowable. I have found the statement of Dragendorff [†] to be true, that sulphuric acid absorbs arseniuretted hydrogen. This is assumed by Janowsky [‡] to be due to decomposition into arsenic and hydrogen, but no proof is given. Dragendorff [†] quotes the suggestion of Otto,[§] that a small amount of fused potassic hydroxide be placed before the fused calcic chloride, in order to absorb any sulphuric acid which might be carried over, it being possible that the acid might act on the calcic chloride, giving hydrochloric acid, which might form arsenious chloride and thus cause loss of arsenic. The potassic hydroxide would also hold back sulphuretted hydrogen. It is well known that potassic hydroxide absorbs antimoniuretted hydrogen, and it has been recently shown by Kuhn and Saeger,[‖] as well as by Headden and Sadler,[*] that arseniuretted hydrogen is also absorbed by it. There is, however, no need of its use as a precaution against either of the contingencies mentioned above.

Lyttkens [¶] considers sulphuric acid to be a better drying agent than calcic chloride, and Lenz [**] agrees with him, but neither shows that there is no loss of arsenic attending its use.

As to Headden and Sadler's [*] statement, unsupported by analysis of the calcic chloride used, that fused calcic chloride holds back arsenic when moist, I have never met with any indication that there was danger of loss from this source.

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[*] Loc. cit.

[†] Ermittelung von Giften, 2te Aufl., p. 336.

[‡] Ber. d. deutsch. chem. Gesell., VI. 216.

[§] Ausmittelung der Gifte.

[‖] Loc. cit.

[¶] Loc. cit.

[**] Loc. cit.

b. Impurities in the Glass of the Deposition Tube. — The errors resulting from the presence of lead and arsenic in glass have been frequently mentioned. The presence of lead in any hard glass fit for use is scarcely probable. The formation of a mirror from either of these sources would however be detected at the start, and the glass rejected at once. I have not found any case of error attributable to impurities in the glass.

c. Temperature of the Reduction Flask. — Dragendorff[*] quotes Kolbe[†] as having shown that sulphuretted hydrogen is always formed by the action of sulphuric acid on zinc, if the reaction temperature exceeds 30°, and recommends on this account that the flask be cooled. The quotation is misleading. What Kolbe showed, and Fordos and Gélis[‡] called attention to the same point some time before Kolbe, was, that if strong acid be added to the flask to increase the action, there was reduction of the acid at the temperature mentioned. With acid diluted with two parts of water no reduction took place. As one would hardly add strong acid to the flask, the danger of formation of sulphuretted hydrogen from mere action of the acid on the zinc is not to be feared. Yet it is necessary to keep the flask cool in some such manner as suggested, if only to prevent too violent action of the acid which may occur from accidental presence of organic matter.

d. Necessity of boiling the Char with Water. — The formation of a "sulphur mirror" is often met with, due to the decomposition of sulphuretted hydrogen at the heating place. Then, too, Brunn[§] has lately shown that sulphuretted hydrogen and arseniuretted hydrogen form, when heated, hydrogen and arsenious sulphide. The necessity of boiling the char with water is therefore evident, in order that no sulphur dioxide be left in the extract to be reduced by the nascent hydrogen.

e. Beginning of Heating. — If the tube be heated as soon as the hydrogen is lighted, the small amount of oxygen left in the flask causes the formation of water in the deposition tube. This can be avoided, if desired, by waiting a few minutes before setting the lamp under the tube.

f. Rapidity of Gas flow and Amount of Heat. — In the method of Chittenden and Donaldson it is necessary to guard against too rapid evolution of gas, and the heating surface must be very great in order that no arseniuretted hydrogen shall escape decomposition. In this method, the amount of heating surface need not be greater than that given by a good burner, and I have assured myself by direct experiment that no arsenic escapes under the ordinary conditions when the size of the mirror is not above 0.06 mgr. It is necessary, however, for the stream of gas to be slow and regular. Hence the disadvantage of organic matter in the extract, causing an increased and irregular flow of gas.

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[*] Loc. cit., p. 336.

[†] Ann. d. Chem. u. Pharm., CXIX. 174.

[‡] Comptes Rendus, XIII. 437.

[§] Ber. d. deutsch. chem. Gesell., XXII. 3202.

6. The following table contains some analyses, taken at random, illustrative of the method.

	Sq. Cm taken.	Grams Extract.	Gr. Extract taken.	Mirror obtained Mgr. As_2O_3.	Mgr. As_2O_3 found.	Mgr. As_2O_3 found per Sq. Meter.
1 . .	100	33.17	33.17	0.030	0.030	3.0
2 . .	100	32.27	6.00	0.017	0.094	9.4
			5.81	0.015	0.083	8.3
3 . .	100	31.84	5.66	0.045	0.253	25.3
			1.90	0.015	0.251	25.1
4 . .	25	29.69	2.64	0.016	0.179	71.9
			2.65	0.017	0.191	76.2
5 . .	111.15	33.66	0.78	0.035	1.510	136.0
			0.46	0.020	1.460	132.0
6 . .	25	30.67	1.01	0.040	1.214	485.6
			2.08	0.080	1.180	472.0
7 . .	12	28.83	0.48	0.030	1.802	1502.0
			0.61	0.043	2.032	1693.0

7. *Comparison of Results obtained by the Berzelius-Marsh Process with those obtained by other Methods of Analysis.* — In order to test the availability of the process, it became necessary to analyze, by one of the general quantitative methods, some of the papers which had been analyzed by the Berzelius-Marsh method. In the analyses given below, the eventual determination was made by an approximately hundredth normal solution of iodine, and, when necessary, titrating back with a sodic thiosulphate solution of corresponding strength. I find a similar method to have been proposed some time ago by Holthof.* Considerable difficulty was met with at first in finding a suitable method of getting the arsenic from the paper into proper state for titration. A measured piece of paper (100–400 sq. cm.) was treated on a porcelain plate with a strong solution of

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* Fresen. Zeitschr., XXIII. 378.

potassic nitrate, dried on the plate, burned over the plate, and the residue washed off into an evaporating dish. The residue was then treated with about 5 c. c. strong sulphuric acid and evaporated until sulphuric acid fumes appeared. To insure the complete expulsion of nitric and nitrous acids, the mass was boiled down again, after addition of a little water. It was then taken up with hot water, filtered, and washed with hot water. The filtrate was kept at 60–70° for half an hour, and sulphur dioxide passed through. After boiling the reduced solution in the flask until sulphur dioxide was expelled, it was made alkaline with sodic bicarbonate, cooled, and titrated. The results obtained were far from satisfactory, but the analyses agreed closely in three cases, which are given below. (Papers numbered 111, 395, and 42 in final table.)

Next, instead of ignition with potassic nitrate, the paper was treated exactly as in the Berzelius-Marsh method, with nitrosulphuric acid (1–30), taking care to get rid of all nitric and nitrous acids. The extract was reduced at 60–70° by sulphur dioxide, the excess of the latter driven off by boiling, and the cooled solution made alkaline with sodic bicarbonate, and titrated. In one case the arsenic was precipitated from the extract by sulphuretted hydrogen, and the arsenious sulphide converted to arsenious acid, and titrated. The amount of time required for this, however, offset any advantage from it. Although by care this method can be employed, yet the details require much time and the chances for error are many. Duplicate analyses agreed closely in two cases which are given below. (Papers numbered 194 and 155 in final table).

The method finally used was adapted from the well known process of Schneider* and Fyfe.† A measured quantity of paper was cut into small pieces and placed in a 500 c. c. distilling flask connected with a cooler. Attached to the latter was a receiver with a second tubulus carrying a long tube which served as an air cooler. About 100 c. c. of hydrochloric acid, diluted one half, were added to the flask, and the mixture distilled, slowly, almost to dryness. It was found by trial, that in nearly every case all the arsenic came over in one distillation, and, if not, that a mere trace was left in the residue. The distillate was transferred to a flask, potassic chlorate added, the solution boiled down one half, transferred to an evaporating dish, and evaporated to dryness, with the addition of a few drops of strong sulphuric acid. The residue was generally white. If dark, from presence of volatile organic matter not destroyed by the potassic chlorate, the addition of a few drops of strong nitric acid and evaporation expelled the organic matter. The residue was then washed into a flask with about 50 c. c. water, and reduced and titrated as in the previous cases.

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* Jahrb. d. Chem., 1851, p. 630.

† Jour. f. prakt. Chem., LV. 103.

The method was tested by the following analyses of filter paper to which known amounts of arsenic were added, 200 sq. cm. of paper being used in each case.

	Mgr. As_2O_3 taken.	C.c. Iodine used. 1 c.c.=0.9815 mgr. As_2O_3.	Mgr. As_2O_3 found.	Per Cent As_2O_3 found.
1 *a*	5	5.1	5.01	102.1
1 *b*	5	5.3	5.20	
2 *a*	5	5.0	4.91	100.1
2 *b*	5	5.2	5.10	
3 *a*	25	25.1	24.64	98.4
3 *b*	25	25.0	24.54	

The residues from the distillations in the last analyses were, after the addition of a few drops of nitric acid, charred with sulphuric acid and "marshed," giving mirrors corresponding to 0.015 mgr. and 0.02 mgr. respectively, showing that a mere trace was left in the flasks.

The following papers were analyzed by this method.

Number of Paper.	Sq. Cm. taken.	C.c. Iodine used. 1 c.c.=0.9815 Mgr.As_2O_3.	Mgr. As_2O_3 found per Sq. Meter.
194	200	17.20	844.00
194	200	17.30	849.00
406	400	3.10	76.07
406	400	3.00	73.61
39	400	2.80	68.71
39	400	2.70	66.25
392	380	1.80	46.50
393	400	0.38	9.33
393	400	0.36	8.83
359	400	1.30	31.90
359	400	1.10	27.00

Finally, the following table shows the comparison of the results obtained by the volumetric method with those obtained on the same papers by the Berzelius-Marsh method. The first two columns compare the results in milligrams per square meter, and the second two in grains per square yard. Each result is the mean of two, unless specified.

Number of Paper.	Mgr. As_2O_3 per Sq. Meter.		Grains per Sq. Yard.	
	Berz. Marsh.	Volumetric.	Berz. Marsh.	Volumetric.
393	8.8	9.1	0.11	0.12
359	24.0	29.5	0.31	0.38
392	46.8	46.5*	0.60	0.60*
39	64.9	67.5	0.83	0.86
406	72.8	74.9	0.94	0.96
111	110.4	108.7	1.42	1.39
395‡	193.0	210.4	2.47	2.69
42	478.8	421.8	6.13	5.40
194	842.0	832.7†	10.78	10.66†
155	1527.1	1478.5	19.55	18.93

* One determination, † Four determinations. ‡ 395 was a piece of "Turkey red" cloth.

Before the above described method was worked out, it was thought that it would give merely an approximation of the amount of arsenic in wall papers and fabrics, which would allow one, for instance, to pass judgment on the articles from a sanitary standpoint. Not only, as will be seen from the table, does the method give an approximation to the actual amount when ordinarily conducted, but with care it can be made to give results worthy of comparison with other quantitative methods. The greatest error occurs naturally in the estimation of large amounts, but in this case an approximation would answer until a more exact determination was called for.

The process will, I think, be also found of great value in toxicological work, not only as a rapid means of determining the quantity of arsenic present, and as a check on other methods, but also as the only means of accurately determining the amount when the arsenic is present in minute quantity. In such work the organic matter would not generally be charred, but the arsenic would be extracted by the method of distillation. I hope to investigate the extension of the method to toxicological work.

The limit of arsenic that I have been able to detect with certainty by the Berzelius-Marsh method is 0.001 mgr. As_2O_3 or 0.0007 mgr. As. I shall not here take up the much discussed question of the delicacy of this as compared with other methods, but I think it will be agreed that no other method enables one to determine quantitatively such small amounts.

In conclusion, I have to thank my assistant, Mr. Charles Walker, very sincerely for his valuable services in most of the analytical work of this paper.

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